

Determination of Pesticides in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography

New York State Food Laboratory
Debra Oglesby, Robert Sheridan, John Meola and Roger Pollman
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A method was developed based on a United States Geological Survey (USGS) method (1) to determine pesticides in drinking water. A mixed mode polymeric solid phase extraction cartridge is used to isolate pesticides from drinking water. This cartridge was chosen over the referenced reverse-phase cartridge because it has both reverse-phase and cation-exchange functionalities. Residual chlorine is removed from the water prior to extraction and methanol is added to improve the overall recoveries. Pesticides are eluted with a mixture of hexane/isopropanol followed by methanol. Samples are analyzed by capillary column gas chromatography (GC). Organophosphate pesticides and their metabolites are identified and quantitated using a flame photometric detector (FPD) and confirmed using gas chromatography/mass spectrometry (GC/MS) with selected-ion monitoring (SIM). Chlorinated pesticides and other non-specific compounds are identified, quantitated and confirmed using gas chromatography /second order mass spectroscopy (GC/MS/MS).

Reagents

- Hexane, J. T. Baker, "Ultra Resi-analyzed"
- Isopropanol, J. T. Baker, "Baker analyzed"
- Methanol (MeOH), J. T. Baker, "Baker analyzed" HPLC grade
- Acetone, J. T. Baker, "Ultra Resi-analyzed"
- Toluene, J. T. Baker, "Ultra Resi-analyzed"
- Sodium Thiosulfate, J. T. Baker, "Baker analyzed"
- Nitrogen gas. 99.9% pure
- Distilled De-ionized water (DDI)

Solutions

- Hexane: isopropanol / 3:1 (HIP). Add 1 part isopropanol to 3 parts hexane. Mix well, store in a stoppered glass container.

Apparatus

- Water's Oasis MCX LP Extraction Cartridge, 6cc x 500mg, Water's part # 186000776
- Supelco Visidry attached to nitrogen source
- Zymark TurboVap attached to nitrogen source
- Zymark concentration tubes, 200ml. Tubes are calibrated at 0.5 ml mark.
- Zymark Autotrace workstation
- O-tolidine reagent, commercially available in swimming pool test kits

Precautions

Fire all glassware used in the procedure at 450° C for 2 hrs.

Analytical Instruments

GC/FPD - Hewlett Packard 6890 Dual Column Gas Chromatograph with Flame Photometric Detector.

Column A: J & W DB-1 capillary column, 1.5um film, 0.53mm ID x 30m

Column B: J & W DB-17 capillary column, 1.0um film, 0.53mm ID x 30m

Carrier gas: He, Inlet temp: 225 °C, Det temp: 250 °C

Oven program: Initial temp: 80° C, Initial time: 0.00 °C

<u>Ramp</u>	<u>Rate</u>	<u>Final Temp</u>	<u>Final Time</u>
1	30.00	178	4.0
2	2.00	205	0.0
3	10.00	310	15.0

GC/MS/MS - Varian 3800 Gas Chromatograph with programmable injection unit, Varian Saturn 2000 GC/MS/MS

Column: J & W DB-XLB capillary column, 0.25um film, 0.25mm ID x 30m

Carrier gas: He

Injector program:

<u>Temp (°C)</u>	<u>Rate (°C/Min)</u>	<u>Hold (min)</u>
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53 0.0 0.30

250 200.0 55.00

Oven Program:

<u>Temp (°C)</u>	<u>Rate (°C/Min)</u>	<u>Hold (min)</u>
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55 0.0 2.00

230 10.0 10.00

275 5.0 18.50

GC/MS - Hewlett Packard 6890 Gas Chromatograph with Hewlett Packard 5973 Mass Spectrometer Detector

Column: DB-35 MS capillary column, 0.25um film, 0.25mm ID x 30m

Carrier Gas: He, Inlet temp: 220°C

Oven program: Initial temp: 100°C, Initial time: 2.00min

<u>Ramp</u>	<u>Rate</u>	<u>Final Temp</u>	<u>Final Time</u>
1	10.0	275	18.0

Sample Pickup and Transport

Samples are obtained by personnel at selected municipal water plants. Each sample is collected in a 1000 ml amber glass bottle containing 1 gm of Sodium Thiosulfate and fitted with a Teflon lined screw cap. The sample is refrigerated and transported to the lab within 24 hours of pickup.

Sample Receipt

1. Samples are to be kept refrigerated until the time of analysis.
2. Remove 5ml water and test for residual chlorine with 2 drops O-tolidine reagent.
3. A yellow color indicates the presence of residual chlorine.
4. Add Sodium Thiosulfate in 1gm increments until residual chlorine is absent.
5. Weigh the sample plus the sample bottle.

Analytical Procedure

1. Samples are to be analyzed within three days of sample receipt or within four days of sample pickup.
2. Reweigh sample bottle after sample has been extracted to determine sample weight by difference.
3. Weigh a 6ml x 500mg Oasis MCX SPE cartridge and record weight on cartridge.
4. Preclean the SPE cartridge with 3ml HIP using gravity. Attach cartridge to Supelco Visidry and dry until original weight is attained.
5. Condition the SPE cartridge with 3ml MeOH followed by 3ml DDI. DO NOT ALLOW THE CARTRIDGE TO GO DRY.
6. Attach the conditioned cartridge to the Zymark Autotrace.
7. Add 10 ml MeOH to the 1000ml sample.
8. Add process controls and/or spiking solutions at this step and mix well.

9. Pump water sample through the conditioned cartridge at a flow rate of 25ml/min.
10. Remove cartridge from Zymark and place on Supelco Visidry cartridge with nitrogen until original weight is attained.
11. Elute cartridge by gravity into a 200ml Zymark tube containing 0.5ml Toluene with 10ml HIP followed by 5 ml MeOH.
12. Apply pressure to remove last traces of MeOH from cartridge.
13. Add 10ml Acetone to Zymark tube and concentrate the eluant to <0.5ml.
14. Add an additional 10ml Acetone and concentrate to < 0.5ml.
15. Add 0.5ml Toluene, mix on Vortex and concentrate to 0.5ml. If < 0.5ml, adjust to 0.5ml with toluene.
16. Divide sample between two autosampler vials for GC/FPD and GC/MS/MS analysis.

Zymark Autotrace Cleanup

After each sample has been pumped thru the Zymark Autotrace, clean the components in the following manner

1. Pump 30 ml of a mixture of 10% Toluene, 20% Methylene Chloride and 70% Isopropanol thru the various lines and fittings of the Autotrace at a flow rate of 10ml / min.
2. Pump 30 ml MeOH thru the Autotrace at a flow of 10 ml / min.
3. Pump DDI thru the Autotrace at a flow of 10 ml / min.

Process Control

Isazophos is used as the process control for this extraction. 100ul of a 0.625ppm solution of Isazophos when added to 1000ml sample will result in a concentration of 0.0625 ppb (62.5 ppt) or approximately five times the limit of quantitation(LOQ).

Spike Samples

Place 1000ml of a water sample, known to be free of the pesticides under study, in a clean container. Add 1gm of sodium thiosulfate and mix until dissolved. Add 10ml MeOH and mix. Add 100ul, 200ul, 500ul or 1ml of a prepared solution of the pesticides under study so that the resulting levels of pesticides correspond to 1, 2, 5, or 10 x LOQ. Add 100ul of the process control solution.

Standards

Standards mixes are prepared in acetone to encompass the linear range from 1 x LOQ to 10 x LOQ. Standards for analysis are prepared in toluene by the following procedure:

- Add 0.5 ml of standard to a 10 ml concentrator tube
- Add toluene to the concentrator tube to bring the volume to 1 ml, vortex.
- Place tube in turbopap and bring concentrate to 0.5 ml or less
- Adjust volume to 0.5 ml with toluene

Standard curves are prepared for each group of samples run.

Quantitation

The level of pesticide in each 0.5ml assay solution is determined from standard curves or by direct comparison of standards that fall within +/- 30% of the response of the sample.

$$\text{Sample (ppt)} = \frac{\text{Assay (ppm)} \times 0.5\text{ml} \times 10^6}{\text{WT sample (g)}}$$

References

1. Methods of Analysis by the U. S. Geological Survey National Water Quality Laboratory - Determination of Pesticides in Water by C-18 Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry with Selected Ion Monitoring.
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